

KOKAI PATENT APPLICATION NO. SHO 60-250009

**METHOD FOR PRODUCING A PERFLUOROCARBON POLYMER HAVING
SULFONIC ACID TYPE FUNCTIONAL GROUP**

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METHOD FOR PRODUCING A PERFLUOROCARBON POLYMER HAVING
SULFONIC ACID TYPE FUNCTIONAL GROUP

[*Suruhon'san'gata kan'nohki o yuhsuru pahfuruorokahbon' juhgohtai no seizoh hōuhoh*]

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Specification

1. Title of the invention

Method for producing a perfluorocarbon polymer having sulfonic acid type functional group

2. Claim of the invention

1. A method wherein emulsion copolymerization is performed for a perfluorocarbon monomer having a sulfonic acid type functional group and tetrafluoroethylene in an aqueous medium in the presence of a polymerization initiator, which method of producing a perfluorocarbon polymer having sulfonic acid type functional group is characterized by the fact that emulsion copolymerization is carried out after emulsification is performed for a perfluorocarbon monomer having sulfonic acid type functional group in an aqueous medium in the presence of a fluorine-containing emulsifier as ultrasonic waves are applied to produce a perfluorocarbon polymer copolymerized with a high proportion of the above-mentioned perfluorocarbon monomer having a sulfonic acid type functional group.

2. The method of production described in claim 1 in which the copolymerization ratio of the perfluorocarbon monomer having sulfonic acid type functional group is at least 20 wt%.

3. Detailed description of the invention

The present invention pertains to a method of producing a perfluorocarbon polymer having a sulfonic acid type functional group, and the invention further pertains to a new method capable of producing a sulfonic acid type perfluorocarbon polymer having a high sulfonic acid type monomer content, that is, high ion-exchange capacity, upon performing emulsion copolymerization in an aqueous medium.

In the past, a polymerization system that utilizes a perfluorocarboxylic acid type emulsifier such as $C_7F_{15}COONH_4$ and $C_8F_{17}COONH$ are used for emulsion polymerization of a fluorine-containing monomer such as tetrafluoroethylene in an aqueous medium. For copolymerization of a monomer having a carboxylic acid type functional group such as $CF_2=CFO(CF_2)_3COOCH_3$ and C_2F_4 , a similar perfluorocarboxylic acid type emulsifier is used, and perfluorocarbon polymer with a high ion-exchange capacity is smoothly and efficiently produced by means of emulsion copolymerization in an aqueous medium.

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On the other hand, in order to achieve high ion-exchange capacity in copolymerization of a monomer having a sulfonic acid type monomer such as



and C_2F_4 , etc., a solid polymerization method where a polymerization medium is not used or solution polymerization method where a fluorine type solvent such as trichlorotrifluoroethane is used as a medium is used. A method where emulsion polymerization is performed in an aqueous medium for copolymerization of a sulfonic acid type monomer and C_2F_4 , etc. is known.

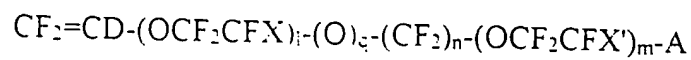
However, according to a study performed by the present inventors, those with a very low ion-exchange capacity alone can be produced in the standard emulsion polymerization that utilizes a conventional sulfonic acid type emulsifier, and that a film capable of achieving 0.5 milli-equivalents gram dry resin used as a cationic ion-exchange film material is not possible.

Based on the above background, and as a result of much research conducted by the present inventors in an effort to produce a sulfonic acid type perfluorocarbon polymer having high ion-exchange capacity based on emulsion copolymerization in an aqueous medium, an interesting factor described below was found. In other words, a newly found knowledge, namely, production of a sulfonic acid type perfluorocarbon polymer with a high ion-exchange capacity can be smoothly and efficiently achieved when a fluorine-containing emulsifier is used and ultrasonic waves are applied and emulsification is performed for a sulfonic acid type monomer in an aqueous medium and emulsion copolymerization is performed with tetrafluoroethylene.

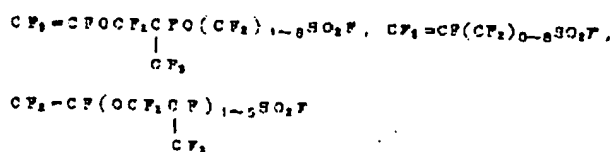
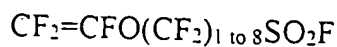
The present invention was accomplished as a result of the above-mentioned newly acquired knowledge and the present invention is to provided a method for production of a perfluorocarbon polymer having a sulfonic acid type functional group characterized by the fact that emulsion copolymerization is performed after emulsification is carried out for a

perfluorocarbon monomer having a sulfonic acid type functional group in an aqueous medium in the presence of a fluorine-containing emulsifier as ultrasonic waves are applied to produce a perfluorocarbon polymer copolymerized with a high proportion of the above-mentioned perfluorocarbon monomer having sulfonic acid type functional group in a method where an emulsion copolymerization is carried out for a perfluorocarbon monomer having sulfonic acid type functional group and tetrafluoroethylene in an aqueous medium in the presence of a polymerization initiator.

For the perfluorocarbon monomer having sulfonic acid type functional group used in the present invention, conventional materials can be used. As a suitable example, a fluoro vinyl compound shown in the following general formula



(Wherein, l is 0-3, m is 0-3, n is 0-12, q is either 0 or 1, X is -F or -CF₃, X' is -F or -CF₃, and A is a sulfonic acid type functional group) can be mentioned. From the standpoint of availability, it is desirable when X and X' are -CF₃, l is either 0 or 1, m is 0, n is 0-8, q is either 0 or 1 and A is -SO₂F from the standpoint of copolymerization reaction, etc. As a typical desirable example of the above-mentioned fluoro vinyl compound,



etc. can be mentioned.

In the present invention, emulsion copolymerization is performed for tetrafluoroethylene and the above-mentioned perfluorocarbon monomer having sulfonic acid type functional group

in an aqueous medium, and in this case, two or more different types of perfluorocarbon monomer having sulfonic acid type functional groups can be used, and furthermore, two or more different types other components, for example, perfluorocarbon monomers containing a carboxylic acid type functional group, divinyl monomers such as $\text{CF}_2=\text{CFORf}$ (Rf is a perfluoroalkyl group with 1-10 carbon atoms) and $\text{CF}_2=\text{CF}-\text{CF}=\text{CF}_2$, and

$\text{CF}_2=\text{CFO}(\text{CF}_2)_1 \text{ to } 4 \text{OCF}=\text{CF}_2$ can be used in combination as well. However, the purpose of the present invention is to produce a perfluorocarbon polymer copolymerized with a high proportion of a perfluorocarbon monomer having sulfonic acid type functional group based on an emulsion copolymerization in an aqueous medium, it is desirable when selection is made for the mixing ratio of the above-mentioned monomers in order to produce a perfluorocarbon polymer having a copolymerization ratio of the aforementioned perfluorocarbon monomer having sulfonic acid type functional group of at least 20 wt%.

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It is further desirable when the selection is made so as to produce a perfluorocarbon polymer having a copolymerization ratio of the aforementioned perfluorocarbon monomer having a sulfonic acid type functional group is in the range of 25 to 60 wt%.

In the present invention, it is important to use a fluorine-containing emulsifier and ultrasonic waves and emulsification of the perfluorocarbon monomer having sulfonic acid type functional group is done in an aqueous medium. After emulsification is done as described above, emulsion copolymerization is carried out with tetrafluoroethylene and other optional monomers. As for the fluorine-containing emulsifier used in this case, perfluorocarbonic acid type emulsifiers commonly used in emulsion copolymerization of tetrafluoroethylene and other fluorine-containing monomers can be used without restriction. For example, carboxylic acids containing perfluoroalkyl groups, or surfactant compounds such as ammonium salts, potassium salts, or sodium salts of a sulfonic acid can be mentioned, and surfactant compounds made of a

compound containing a perfluoropolyether chain can be mentioned as well. In general, the above-mentioned fluorine-containing emulsifier is used in an aqueous medium at a concentration of 0.001 to 5 wt%, preferably, 0.05 to 2.0 wt%.

In general, emulsification based on application of ultrasonic waves is achieved through application of ultrasonic waves of 0.1 to 1000 KHz, preferably, 1 to 100 KHz for 1 to 120 minutes, preferably, 10 to 60 minutes. Furthermore, in emulsification of a perfluorocarbon monomer having sulfonic acid type functional group in an aqueous medium, the above-mentioned fluorine-containing emulsifier is added. In this case, additives such as buffers and molecular weight modifiers commonly used in the emulsion copolymerization may be added before or after application of the ultrasonic waves. In this case, stirring at the time of radiation is not especially limited, and stirring may be omitted. The condition used for emulsification in the presence of the above-mentioned fluorine-containing emulsifier and ultrasonic wave is not especially limited, and a temperature in the range of 5 to 90°C. for example, can be used.

In the present invention, emulsion copolymerization is done with tetrafluoroethylene and other optional monomers after emulsification of the perfluorocarbon monomer having a sulfonic acid type functional group is done in an aqueous medium in the presence of a fluorine-containing emulsifier as ultrasonic waves are applied as described above, and the conditions used in this case are not especially limited.

When the perfluorocarbon polymer having a sulfonic acid type functional group of the present invention is used as an ion-exchange film, the ion-exchange capacity of the polymer can be selected from a wide range of 0.5 to 2.0 milliequivalents/gram dry resin, and when the conditions described below are utilized, the molecular weight of the copolymer produced can be increased even when the ion-exchange capacity is increased, thus, reduction in mechanical properties and wear resistance of the copolymer does not occur. The ion-exchange capacity varies depending on the type of copolymer used and from the standpoint of mechanical properties and electrochemical properties of the polymer used as an ion-exchange resin, at least 0.7

milliequivalents/gram dry resin is desirable and at least 0.8 milliequivalents/gram dry resin is even more desirable. Furthermore, the molecular weight of the perfluorocarbon polymer having sulfonic acid type functional group produced in the present invention is important in relation to the mechanical properties and film formability of the ion-exchange film, and at least 150°C in terms of the value of TQ is suitable, and in the range of 170 to 340°C, especially, 180 to 280°C, is further desirable.

In the specification of the present invention, the term "TQ" is defined as below. That is, the temperature that exhibits a volume flow velocity $100 \text{ mm}^3/\text{sec}$ having an influence on the molecular weight of the copolymer is defined as TQ. In this case, the volume flow velocity is shown in the units of the mm^3/sec of the polymer as melting is performed for the copolymer from an orifice with a diameter of 1 mm and a length of 2 mm at a constant temperature and under a pressure of 30 kg cm^2 . Furthermore, "the ion-exchange capacity" was obtained as shown below.

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In other words, an H-type cationic ion-exchange film is stored in 1N HCl at 60°C for 5 hours so that complete conversion to H-type can be achieved, and a thorough washing is subsequently performed with water to remove residual HCl. Then, 0.5 g of the above-mentioned H-type film is placed in a solution produced by adding 25 ml of water to 25 ml of 0.1N NaOH for 2 days at room temperature. Subsequently, the film was removed and an inverse titration with 0.1N HCl was done to determine the amount of NaOH in the solution.

In the present invention, it is desirable when the copolymerization reaction of a functional group monomer such as sulfonic acid type monomer and tetrafluoroethylene at a weight ratio of the aqueous medium functional monomer of 20/1 or below, preferably, 10/1 or below. When the amount of the aqueous medium used is too high, the copolymer reaction rate is reduced and a long time is required to produce a high copolymer yield. Furthermore, when the amount of the aqueous medium used is too high, a polymer with high molecular weight cannot be achieved when used as a high ion-exchange capacity. In addition, when an excess amount of the aqueous

medium is used, problems described below exist. For example, a large-scale reaction device is required, and workability becomes complicated due to separation and recovery of the copolymer.

Furthermore, it is desirable when copolymerization reaction pressure of at least 2 kg/cm^2 is used in the present invention. When the copolymerization reaction pressure is too low, it is difficult to maintain the copolymerization reaction speed at an adequate level and production of a copolymer with a high molecular weight becomes difficult. Furthermore, when the copolymerization reaction pressure is too low, the ion-exchange capacity of the copolymer produced becomes too high and reduction in mechanical strength and ion-exchange capacity is likely to increase due to an increase in high water absorption. Furthermore, it is desirable when the copolymerization reaction pressure used in this case is 50 kg/cm^2 or below from the standpoint of reactor used or workability. It is possible to use a copolymerization reaction pressure of above the above-mentioned value, but an additional advantage cannot be achieved. Therefore, it is desirable when the copolymerization reaction pressure is selected from a range of 2 to 50 kg/cm^2 , preferably, 4 to 30 kg/cm^2 .

The aforementioned polymerization reaction, etc. are not especially limited in the copolymerization reaction of the present invention and selection can be made from a wide range. For example, the optimum value of the copolymerization reaction temperature is determined by the type of polymerization initiator used and the reaction molar ratio, etc., and in general, too high a temperature or too low a temperature is a disadvantage, thus, the temperature is selected to be in the range of 20 to 90°C , preferably, 30 to 80°C .

For the polymerization initiator used in the present invention, a material that exhibits high activity at the aforementioned suitable reaction temperature is desirable. For example, it is possible to use a highly active ionizing radiation at a temperature of below the room temperature, but in general, use of azo compounds and peroxide compounds are further desirable from the standpoint of industrial application. For examples of the polymerization initiators that can be used effectively in the present invention, diacyl peroxides such as disuccinic acid peroxide,

benzoyl peroxide, lauroyl peroxide and dipentafluoropropionyl peroxide, azo compounds such as 2,2'-azobis(2-amidinopropane)hydrochlorate and azobisisobutyronitrile, peroxide esters such as t-butylperoxyisobutylate, and t-butyl- peroxyvalate, peroxydicarbonate such as diisopropylperoxy- dicarbonate and di-2-ethylhexylperoxydicarbonate, hydroperoxides such as diisopropylbenzene hydroperoxide, inorganic peroxides such as potassium persulfate and ammonium persulfate, and redox thereof can be mentioned.

In the present invention, the concentration of the polymerization initiator used is in the range of 0.0001 to 3 wt%, preferably, in the range of 0.001 to 2 wt%, for the total monomer. It is possible to increase the molecular weight of the copolymer produced by reducing the concentration of the initiator and retention of high ion-exchange capacity can be made possible. When the concentration of the initiator is too high, the molecular weight is likely to be reduced, and production of a copolymer with a high ion-exchange capacity and high molecular weight is less likely to occur.

[p. 5]

Furthermore, a variety of surfactants, dispersants, buffers, molecular weight modifiers, etc. commonly used for emulsion copolymerization in an aqueous medium can be used in this case as well. Furthermore, inert organic solvents known as Freon-type solvents, such as fluoride or hydrogen fluoride type saturated hydrocarbons, may be added as long as the copolymerization reaction of the present invention is not inhibited and the chain transfer ratio is low.

In the present invention, the reaction is carried out in such a manner that the concentration of the copolymer produced is 40 wt% or below, preferably 30 wt% or below, can be achieved. When the concentration is too high, increase in non-uniformity of the copolymer composition and dispersing failure of the latex pose problems.

The sulfonic acid type perfluorocarbon polymer of the present invention can be formed into a film by an appropriate means. For example, the functional group is converted to a sulfonic acid group by means of a hydrolysis reaction and the hydrolysis reaction can be carried out before

or after film formation. In general, it is desirable when a hydrolysis reaction is performed after the film formation. A variety of means can be used for film formation, and for example, known methods such as hot-melt molding, latex molding, and injection molding after dissolving in an appropriate solution can be used. Furthermore, lamination can be carried out with a film having a different ion-exchange capacity or a film having a different functional group such as a carboxylic acid to form two or more layers. Furthermore, reinforcement can be performed with a material such as cloth, fibers, and non-woven fabric.

The ion-exchange film made of the sulfonic acid type perfluorocarbon polymer of the present invention with excellent properties can be used for a variety of applications. For example, the film can be effectively used as a barrier membrane for diffusion dialysis, electrolytic reduction, and fuel cell battery in fields where corrosion resistance is required. In particular, when used as a cation selective barrier film of an alkali electrolyte, high performance can be achieved when laminated with a carboxylic acid type film. For example, when a structure referred to as a two-cell tank in which the anode and cathode are separated by the above-mentioned cationic ion-exchange film to form an anodic cell and a cathodic cell, an alkali chloride solution is supplied to the anodic cell and electrolysis is carried out and an alkali hydroxide is obtained from the cathodic cell; long-term, stable production of sodium hydroxide with a high concentration of at least 30% can be achieved at a high current efficiency and low tank voltage when an electrolysis reaction is carried out at a current density of 5 to 50 A/cm² using a sodium chloride solution with a concentration of at least 2N.

The present invention is further explained in specific terms with working examples below, but needless to say, the present invention is not limited to these working examples.

Working example 1

0.2 g of C₈F₁₇-COONH₄, 0.50 g of Na₂HPO₄·12H₂O and 0.29 g of NaH₂PO₄·2H₂O were dissolved in 100 g of deionized water and 20 g of



was further

added. Subsequently, ultrasonic wave was applied for 15 minutes. For the ultrasonic wave generator, US600 produced by Nihon Seiki Co., Ltd. was used. Furthermore, 0.026 g of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ was added to the above-mentioned solution, and charged to a stainless steel pressure resistant reactor with 0.2-liter capacity, a thorough degassing was performed with liquid nitrogen, and the temperature was adjusted to 57°C , and then, 11 kg/cm^2 of tetrafluoroethylene was charged and the polymerization was initiated. During the course of the reaction, tetrafluoroethylene was supplied from the outside the system and the pressure was maintained constant. After 8 hours, purging was performed for the non-reacting tetrafluoroethylene and the polymerization was completed, the latex produced was collected, washed and dried to produce 11.7 g of copolymer. The ion-exchange capacity of the aforementioned copolymer was 1.08 meq/g. When press molding was performed for the aforementioned copolymer at a temperature of 230°C , a film with a high strength was produced, and when a hydrolysis reaction was performed with a 25% caustic soda solution, a sulfonic acid type ion-exchange film was produced.

When a polymerization reaction and post treatments were performed in the same manner without application of ultrasonic wave, ion-exchange capacity was absent in the copolymer produced.

[p. 6]

Working example 2

An emulsification was performed as in the case of working example 1 with ultrasonic wave, then, the content was transferred to a pressure resistant reactor and the polymerization pressure of tetrafluoroethylene was changed to 8 kg/cm^2 and polymerization was performed in the same manner.

After 8 hours, 7.2 g of copolymer was produced. The ion-exchange capacity of the aforementioned copolymer was 1.28 meq/g. When press molding was performed for the aforementioned copolymer at a temperature of 200°C , an excellent film was produced and when

a hydrolysis reaction was performed, a sulfonic acid type ion-exchange film was produced.

When a polymerization reaction and post treatments were performed in the same manner without application of ultrasonic waves, the ion-exchange capacity achieved was 0.01 meq/g.

Working example 3

In the above-mentioned working example 1, 0.5 g of $C_7F_{15}COONH_4$ was used as an emulsifier, ultrasonic waves were applied for 60 minutes, and application was done as the solution was being chilled and a polymerization reaction was carried out in the same manner.

The ion-exchange capacity of the copolymer produced was 1.13 meq/g.

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